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X-Ray Intensity Fluctuation Spectroscopy Studies on Phase-Ordering Systems

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(Received 16 September 2004; published 9 February 2005)

The order-disorder phase transition in Cu_3Au has been studied by x-ray intensity fluctuation spectroscopy. Following a quench from the high-temperature, disordered phase, the ordering kinetics is well described by a universal scaling form that can be measured by time-resolved (incoherent) x-ray scattering. By using coherent scattering, we have measured the fluctuations about this universal scaling form. In the late stages of the ordering process, these fluctuations give a two-time correlation function $C(q, t_1, t_2)$ which has a scaling form with natural variables $\delta t = |t_1 - t_2|$ and $\bar{t} = \frac{(t_1+t_2)}{2}$. The scaling form crosses over from linear in $\bar{t}$ to $\bar{t}^{1/2}$. These present the first such results for a nonconserved system.

The development of long range order out of a disordered system is a well-known and well studied class of nonequilibrium processes. The time evolution of the order is characterized by one length scale [e.g., an average domain size, $R(t)$] and looks invariant in time when the system is scaled by this characteristic length. The time dependence can often be described by a power law: $R(t) \propto t^n$. This scaling hypothesis has been found to describe correctly the time evolution of a large class of systems and to be independent of many microscopic details of the system. For example, for first-order phase transitions with a nonconserved order parameter, often called model A [1], the growth exponent is found to be $n = 1/2$ while $n = 1/3$ for conserved systems, also called model B. Dynamical scaling appears to well describe the average behavior of these nonequilibrium systems. A natural question then arises as to whether dynamical scaling will also describe fluctuations about this average behavior.

X-ray intensity fluctuation spectroscopy (XIFS) is an ideal way to perform direct measurements of the dynamics of fluctuations in condensed matter systems at atomic length scales. Over the past few years, XIFS has been used to study the equilibrium dynamics in a large number of hard- and soft-condensed matter systems [2]. However, there were many fewer attempts to extend XIFS and study nonequilibrium dynamics. The use of two-time correlation functions as proposed in [3,4], to study the dynamics of fluctuations, has proven to be useful in studies of phase separation experiments (model B) [5,6]. This Letter presents the first measurements of two-time correlation functions and their temperature dependence in systems undergoing first-order phase transition with nonconserved order parameter (model A).

The Cu_3Au alloy is a real workhorse for studies on phase transitions [7]. At high temperatures, the alloy has a fcc lattice with each site randomly occupied by either a Cu or Au atom. Below the critical temperature $T_c \approx 383\,^\circ C$ the

system develops a $L1_2$ ordered structure. The Au atoms occupy the corners of a conventional unit cell while the Cu atoms place themselves at the face sites. However, since the "corner" can be chosen in four different ways, the ground state is fourfold degenerate [7–9]. Ordered domains in different ground states are separated by antiphase domain walls. Because of the complex domain structure, the superlattice reflections from Cu_3Au are not isotropic (see Fig. 1). Low-energy, in-plane half-diagonal glides form so-called type-1 antiphase domain walls that are measured by the large axis of the ellipse-shaped reflections while higher energy type-2 domain walls are formed by out-of-plane half-diagonal glides and are measured by the small axis of the ellipse. Following a temperature quench, droplets of the ordered phase in any of the four allowed ground states appear and grow in a matrix of disordered phase. Eventually the domains meet and the system is composed of ordered domains in different ground states separated by antiphase domain walls. At this point the coarsening regime begins and the growth of the average domain size is well described by a $R(t) \propto t^{1/2}$ scaling law. Earlier studies of this process used time-resolved x-ray scattering to probe both the early nucleation and growth [10] and the coarsening [8] regimes.
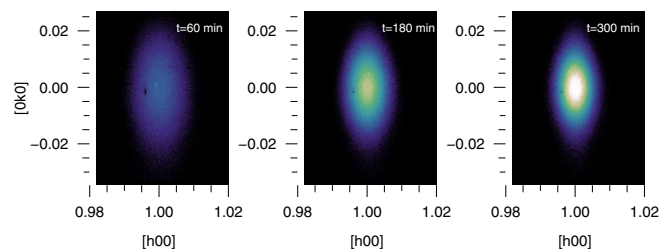

FIG. 1 (color online). Time evolution of the [100] superlattice peak after a quench from 425 to 370 °C.

The experiments were performed using partially coherent x rays at beam line 8-ID of the Advanced Photon Source. A thin diamond crystal monochromator is used to produce 7.66 keV x rays having a relative bandwidth $\Delta\lambda/\lambda = 6.2 \times 10^{-5}$ and a flux of $\sim 5 \times 10^{12}$ photons per second for a storage ring current of 100 mA. A transversely coherent beam was produced using slits with highly polished edges set to a horizontal aperture of 5 μm and a vertical aperture of 10 μm. The scattered x rays around the [100] superlattice reflection of a Cu_3Au single crystal were recorded by a area direct-detection charge-coupled device (CCD) with 22 μm square pixels located 1.20 m from the sample.

The sample vacuum furnace consists of a pyrolytic-graphite heater mounted on a water-cooled Cu heat sink. This arrangement gives sufficient cooling power to achieve cooling rates of about 1 °C/s as measured by a thermocouple mounted on the sample surface. Fast temperature quenches without any significant undershooting were performed using a temperature controller that combines proportional-integral-derivative feedback, thermal modeling (feedforward), and Kalman filtering of the temperature readings [11]. In a typical experiment, the sample was held at $\sim$425 °C and rapidly quenched (within 1 min) to a temperature below T_c, where it was held for a few hours.

The speckled aspect of the diffraction pattern is a consequence of the coherent illumination of the sample. A normalized intensity fluctuation can be defined as

$$D(\mathbf{q}, t) = \frac{I(\mathbf{q}, t) - \langle I(\mathbf{q}, t) \rangle}{\langle I(\mathbf{q}, t) \rangle}. \qquad (1)$$

The main problem associated with performing XIFS measurements in nonequilibrium systems comes with the need to evaluate the average scattered intensity $\langle I(\mathbf{q}, t) \rangle$, which measures the ensemble averaged structure factor that would be obtained from incoherent x-ray diffraction. In an equilibrium system $\langle I(\mathbf{q}, t) \rangle$ is expected to be constant in time and can be evaluated simply by averaging $I(\mathbf{q}, t)$ over a long enough time interval. However, in a nonequilibrium system $\langle I(\mathbf{q}, t) \rangle$ changes with time and separating the intensity fluctuations from this changing average is a nontrivial issue.

In isotropic systems, $\langle I(\mathbf{q}, t) \rangle$ can be evaluated by averaging over intensities at constant q [5,6]. For our particular system, this approach is not possible because of the anisotropy of the superlattice reflections in Cu_3Au. The incoherent (average) scattered intensity $\langle I(\mathbf{q}, t) \rangle$ could also be evaluated by least-squares fitting various analytical forms for $I(\mathbf{q}, t)$ to the measured intensities. Fits with 2D Gaussian functions, with forms resulting from a Hendricks-Teller model for the scattering from Cu_3Au [10] or with squared Lorentzian functions work generally well but, as for any least-squares fits, some regions are affected by small systematic errors. The systematic errors can significantly affect the measured fluctuations, espe-

cially at high q levels where the scattered intensity is low, artificially increasing the fluctuation correlation functions. In order to take full advantage of the whole q range allowed by the CCD detector, the average structure factor $\langle I(\mathbf{q}, t) \rangle$ was calculated by using a two-dimensional Sawitzky-Golay (SG) smoothing filter [12].

The scaling behavior of the average structure factor is shown in Fig. 2. The normalized intensity $\frac{I}{I_{\max}}$ follows a universal curve if plotted against a scaled position $dq t^{1/2}$ (here, dq measures the distance from the peak center in the radial direction), which means that properties of the system scale with a single characteristic domain size R and that this length grows as $t^{1/2}$. However, this scaling behavior is not temperature independent. The inset in Fig. 2 shows the average domain size, calculated as the inverse of the FWHM of the Bragg peaks, as a function of time for two different temperatures. The coarsening of the antiphase domains are driven by the reduction of the surface energy associated with the domain walls. The temperature dependence is the result of the competition between a higher free energy difference for a deeper quench and a reduced diffusion constant due to the lower temperature. In the 360–375 °C temperature range, the process is diffusion limited. The growth rate is slower for deeper quenches.

With $\langle I(\mathbf{q}, t) \rangle$ evaluated by the SG smoothing filter, the intensity fluctuations can be calculated from Eq. (1). The two-time correlation function is defined as the covariance
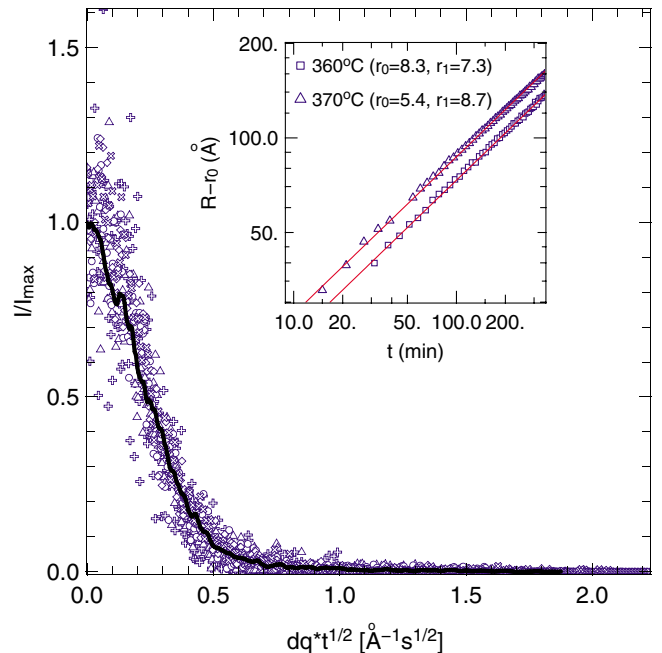

FIG. 2 (color online). Rescaled intensity vs rescaled radial position at five different times, and the scaled SG estimate for the incoherent scattering (solid line). The inset shows fits for the characteristic domain size (1/FWHM) with the form $R = r_0 + r_1 t^{1/2}$.

of the scattered intensity:

$$C(\mathbf{q}, t_1, t_2) = \langle D(\mathbf{q}, t_1) D(\mathbf{q}, t_2) \rangle_{\text{equivalent } q}. \quad (2)$$

The averages were calculated over small areas of 10×10 pixels, considered to map all into the same $\mathbf{q}$. Contour plots of the two-time correlation functions for two values of q in the radial direction and two different temperatures are shown in Fig. 3. Following the analysis of [3,4] the two-time correlation functions are expressed in terms of a natural set of variables, the average time $\bar{t} = (t_1 + t_2)/2$ and the time difference $\delta t = |t_1 - t_2|$. A constant value of $\bar{t}$ corresponds to a line perpendicular to the $t_1 = t_2$ diagonal and δt measures the distance from the equal-time diagonal (in units of time) along such a line. A correlation time τ can be defined as the time difference δt, for which the correlation function decreases to $1/2$ of its equal-time value. The correlation functions along the $t_1 = t_2$ diagonal measure the coherence of the beam but also contain a term from the Poisson noise in photon counting which affects their values. As a consequence, only the nondiagonal, $t_1 \neq t_2$, elements were used by the fitting routines described below.

The large $\bar{t}$ asymptotic limit of the normalized correlation function can be obtained in an explicit form [3]. For a three-dimensional system, the predicted form is

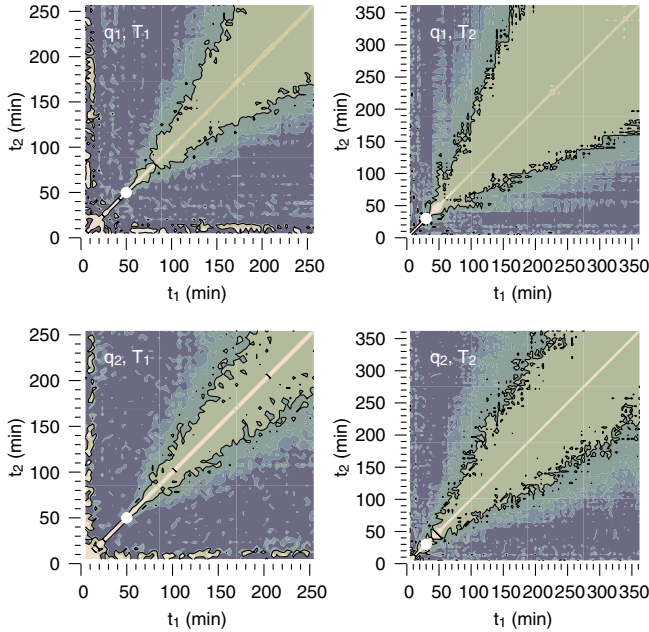$$C_{\text{norm}}(z) = [z^2 K_2(z)/2]^2. \quad (3)$$

FIG. 3 (color online). Two-time correlation functions, $C(\mathbf{q}, t_1, t_2)$, calculated for $\mathbf{q}_1 = [1.002, 0.000, 0]$, $\mathbf{q}_2 = [1.003, 0.001, 0]$, $T_1 = 370\,°C$, and $T_2 = 375\,°C$. Contour levels are 0.001, 0.002, 0.004, 0.008, and 0.016. The black contour corresponds to a level of 0.004 which is half the coherence factor $\beta \simeq 0.008$.

The scaling variable is $z = A \delta t/\bar{t}^{1/2}$, where A makes the variable dimensionless and $K_2(z)$ is a modified Bessel function of the second kind. Fits of the two-time correlation functions were done using an approximation for Eq. (3) given in [6]. The results for the $360\,°C$ temperature quench are shown in Fig. 4.

The scaling behavior of the two-time correlation functions is shown in Fig. 5. As predicted in [3], the rescaled correlation times $dq^2\tau$ plotted against the rescaled average time $dq^2\bar{t}$ obey a scaling law with asymptotic limits $\sim\bar{t}$ in the low $\bar{t}$ limit and $\sim\bar{t}^{1/2}$ in the high $\bar{t}$ limit. In order to make this scaling form work, the time origin was shifted by some temperature-dependent amount t_0, marked by the white dots in two-time correlation plots (Fig. 3). At earlier times the two-time correlations are zero, or smaller than the resolution (of the order of 1–3 min). These rather large "incubation times" for the two-time scaling behavior are a new and an intriguing piece of evidence that poses more experimental and theoretical challenges in the study of the early-time behavior of the order-disorder phase transition in Cu$_3$Au. Our detailed analysis of the "one-time" structure factor $\langle I(q, t) \rangle$ [13] shows a small shift in the Bragg peak center and a subtle change in the aspect ratio of the [100] superstructure peak happening during the early stages of the ordering process, for times comparable to t_0. The different behavior of the two-time correlation functions during the same time interval is probably a consequence of this and reflects a more subtle relaxation mechanism, involving some difference between the two types of antiphase domain walls.

With the appropriate choice of time origin, t_0, the scaling form in Eq. (3) becomes temperature independent. The
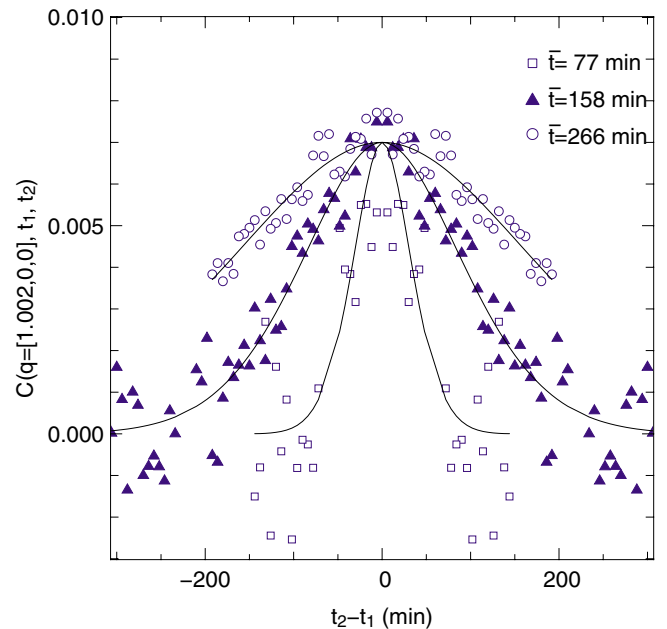

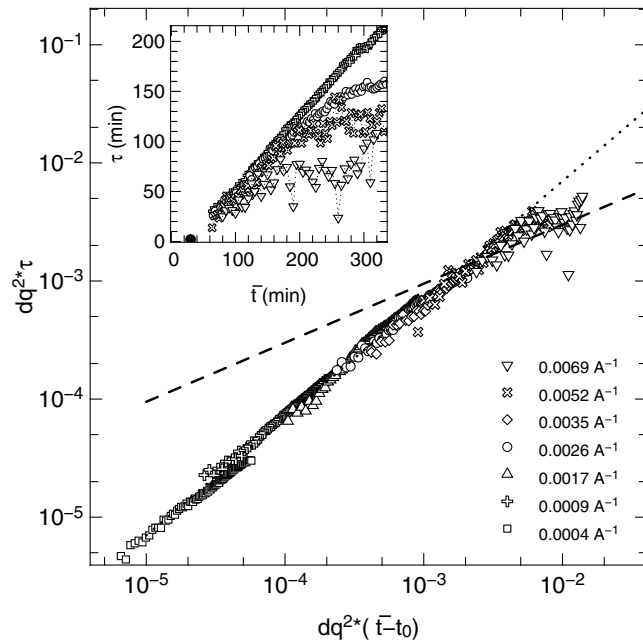FIG. 4 (color online). Least-squares fits of the two-time correlation functions.

FIG. 5. Rescaled, fitted correlation times for all q values along a radial scan. The dotted line has slope 1 and the dashed line has slope $1/2$. The nonscaled correlation times for some values of q are shown in the inset.

temperature dependence comes only through the characteristic time t_0 and is qualitatively different from the temperature dependence of the one-time quantities. The characteristic time t_0 is longest ($t_0 \sim 50$ min) for the shallowest quench (375 °C) and reaches a plateau for temperatures ranging from 360–370 °C ($t_0 \sim 28$–30 min). Like the temperature dependence of the one-time quantities, this is due to the competition between an increased thermodynamic driving force for structural relaxation caused by a deeper quench and a reduced atomic mobility at lower temperatures. The difference comes perhaps from the fact that the predominant thermodynamic force for domain growth in the coarsening regime is the surface free energy reduction, while the density-density fluctuations measured by the two-time functions are driven by the reduction of both bulk and surface free energy.

The nature of the fluctuations about the average scaling behavior are quite different from equilibrium fluctuations. Models for growth in ordering systems show that large domains grow at the expense of small domains. This behavior is nicely captured by the two-time correlation functions and in the scaling which shows that fluctuation correlation time grows with time. Cu_3Au was chosen because it represents a model system in which dynamical scaling for the average domain size works well. It will be most interesting to measure the two-time correlation function in a broader range of nonequilibrium systems.

In conclusion, most previous work on dynamical scaling was based on measurements of the average behavior. Our results emphasize that fluctutations about the average behavior also follow dynamical scaling. These are the first experimental confirmation of scaling of two-time correlation functions in a first-order phase transition with the nonconserved order parameter (model A).

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